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(54) HYDROGEN OCCLUDING MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain hydrogen occluding material having a large hydrogen storage capacity per volume.

SOLUTION: In this hydrogen occluding material, the specific surface area of amorphous carbon which has a layer structure including carbon crystallites of hydrocarbon is 400 m²/g or less, the ratio H/C of the number of hydrogen atom to that of carbon atom is in the range of 0.05-0.45, and hydrogen is occluded between layers of the carbon crystallites or between terminals of the crystallites of the amorphous carbon. Further, in order to increase the hydrogen storage capacity per volume, it is desirable to make the interlayer distance d002 of the face (002) of the amorphous carbon 0.4 nm or more, to use the amorphous carbon which is obtained by executing heat treatment of raw coke produced from high molecular compounds, natural polymers,

petroleum or coal, at the temperature of 500-900°C, to execute the heat treatment in an inactive atmosphere and so on.

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CLAIMS

[Claim(s)]
[Claim 1] the specific surface area of the amorphous carbon of the layer structure containing the carbon microcrystal of a hydrocarbon -- below 400m²/g -- it is -- the ratio of the number of hydrogen atoms, and a carbon atomic number -- the hydrogen absorption ingredient characterized by H/C being in or more 0.05 0.45 or less range, and coming to carry out occlusion of the hydrogen between the carbon microcrystal layers of this amorphous carbon, or between microcrystal ends.
[Claim 2] The hydrogen absorption ingredient according to claim 1 characterized by the distance between carbon microcrystal layers of said amorphous carbon being 0.4nm or more.
[Claim 3] Said amorphous carbon is a hydrogen absorption ingredient according to claim 1 or 2 which heat-treats one sort or two sorts or more of ingredients chosen from the raw coke obtained from a high molecular compound, naturally-occurring polymers, petroleum, or coal in 500-degree-C or more temperature requirement 900-degrees C or less, and is obtained.
[Claim 4] It is the hydrogen absorption ingredient according to claim 3 characterized by performing said heat treatment under an inert atmosphere.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the hydrogen absorption ingredient which comes to carry out occlusion of the hydrogen to a carbonaceous ingredient in more detail about a hydrogen absorption ingredient.

[0002]

[Description of the Prior Art] Hydrogen is an important chemistry raw material used for synthetic chemistry industry, petroleum refining, etc. so much. On the other hand, in order to solve future energy problems and environmental problem, it is thought that the hydrogen use technique as clean energy occupies an important location, and researches and developments are actively furthered in every direction of hydrogen manufacture, storage and transportation, and a conversion technique. In the occlusion and the transportation technique of hydrogen, the so-called hydrogen storing metal alloy is considered to play main roles except for very large-scale objects, such as a hydrogen tank. It is required that hydrogen should be especially supplied to a cell etc. in migration media, such as a fuel cell powered vehicle.

[0003] It is because it is not adapted to such a demand with the high-pressure hydrogen chemical cylinder or liquefaction hydrogen bomb which are the existing technique. Although it is an alloy, when degradation (the pulverization of an alloy and structural change) by the weight (the amount of occlusion per unit weight is small) of a reason and the repeat of occlusion-emission and a rare metal are included also in the hydrogen storing metal alloy considered to be the leading role in such a scene, the technical problem which should be conquered has much the resource reservation etc.

[0004] Under such a background, the activated carbon more than 1000m²/g has been proposed for specific surface area as a hydrogen absorption ingredient with the lightweight and abundant amounts of resources (refer to Patent Publication Heisei No. 504394 [eight to] official report).

[0005]

[Problem(s) to be Solved by the Invention] However, since the hydrogen absorption ingredient which consists of activated carbon has the low bulk density of activated carbon, there are comparatively few hydrogen storage capacities per volume. Therefore, for example, when it used as fuel sources of an automotive fuel cell, there was a problem that sufficient mileage was not obtained.

[0006] The technical problem which is going to solve this invention is to be able to expect the use as fuel sources of such an automotive fuel cell etc., utilize a carbon material with the lightweight and abundant amounts of resources, and offer a hydrogen absorption ingredient with the big hydrogen storage capacity per volume.

[0007]

[Means for Solving the Problem] the specific surface area of the amorphous carbon of the layer structure with which the hydrogen absorption ingredient of this invention according to claim 1 contains the carbon microcrystal of a hydrocarbon in order to solve this technical problem -- below 400m²/g -- it is -- the ratio of the number of hydrogen atoms, and a carbon atomic number -- H/C is in or more 0.05 0.45 or less range, and makes it a summary to come to carry out occlusion of the hydrogen between the carbon microcrystal layers of this amorphous carbon, or between microcrystal ends.

[0008] The carbon microcrystal of the above-mentioned amorphous carbon mainly consists of a hydrocarbon, it has the six membered ring reticulated planar structure, and the part has the same layer structure as a crystal-like graphite. Moreover, the end of the above-mentioned microcrystal will be together joined by hydrogen to carbon, and occlusion of the hydrogen content child will be carried out also to the mold cavity formed between the ends of carbon microcrystal. For this reason, compared with the activated

carbon with which occlusion of the hydrogen is carried out to a carbon front face by the conventional physical adsorption, the amorphous carbon concerning this invention can carry out occlusion of more hydrogen.

[0009] In this case, specific surface area of the amorphous carbon of this invention was made or less [400m] into two. Since it is small compared with usual activated carbon, bulk density becomes large and this value can make [many] the hydrogen storage capacity per volume.

[0010] moreover, the ratio of the number of hydrogen atoms in amorphous carbon, and a carbon atomic number -- when H/C (the number of hydrogen atoms / carbon atomic number) becomes smaller than 0.05, there is a possibility that the hydrogen storage capacity generated in the end of carbon microcrystal at the time of hydrogen absorption may become small. On the other hand, if H/C (the number of hydrogen atoms / carbon atomic number) exceeds 0.45, the carbonaceous six membered ring reticulated planar structure will become extremely small, and hydrogen absorption sites will decrease in number.

[0011] And in this invention, a thing [that the distance between carbon microcrystal layers of said amorphous carbon is 0.4nm or more] according to claim 2 is [like] desirable.

[0012] When the distance between layers sets to 0.4nm or more, between layers, occlusion of the hydrogen content child is carried out smoothly, and the amount of occlusion increases. Although there is no limit in the upper limit of the distance between layers, composition of the carbon which generally has between layers 0.6nm or more is difficult.

[0013] Moreover, in this invention, said amorphous carbon is obtained as a suitable thing like by heat-treating one sort or two sorts or more of ingredients chosen from the raw coke according to claim 3 obtained from a high molecular compound, naturally-occurring polymers, petroleum, or coal in 500-degree-C or more temperature requirement 900 degrees C or less.

[0014] Since the carbon condensed ring used as the site which carries out occlusion of the hydrogen does not generate when the above-mentioned heat treatment temperature is less than 500 degrees C, a hydrogen storage capacity will fall greatly. Moreover, when the above-mentioned heat treatment temperature exceeds 900 degrees C, H/C mentioned above becomes smaller than 0.05, and there is a possibility that the amount of occlusion generated in the end of carbon microcrystal at the time of hydrogen absorption may become small. The minimum of still more desirable heat treatment temperature is 600 degrees C, and an upper limit is 800 degrees C.

[0015] A thing [performing the above-mentioned heating in an inert atmosphere like in this invention] according to claim 4 is still more desirable. Thereby, oxidation of a carbon raw material can be prevented and amorphous carbon can be obtained. In addition, as the above-mentioned inert atmosphere, the ambient atmosphere which consists of a vacuum ambient atmosphere, rare gas, and N₂ grade can be mentioned, for example. Moreover, although especially the desirable time amount of heating is not limited, especially the range of for [30 minutes] - 8 hours is desirable also in it.

[0016]

[Embodiment of the Invention] The example of this invention is explained below at a detail.

[0017] (Example 1) {Y. which compounded poly acene system oligomer using the Rigaku high-pressure reactor by the high pressure polymerization (0.1GPa, 250 degrees C, 5h) of diphenyl diacetylene Kojima, M.Tsuji, T.Matsuoka, H.Takahashi, Macromolecules, 27, 3735(1994)}. The oligomer obtained in this way was set to the electric furnace, heat-treatment of 5 hours was performed with the sink at the programming rate of 20 degrees C / min, and each temperature of 600,800 degrees C, and natural radiationnal cooling of the Ar gas of 11. / min was carried out after that. The obtained amorphous carbon was put into the container made from agate, and was ground.

[0018] (Example 1 of a comparison) Three kinds (trade name: M15, M20, M30) of activated carbon of Osaka Gas chemical ** was used.

[0019] Since specific surface area and a hydrogen storage capacity were measured about two kinds (600 degrees C, 800 degrees C) of amorphous carbon of the above-mentioned example 1, and three kinds (trade name: M15, M20, M30) of activated carbon of the example 1 of a comparison, the result is shown in Table 1. In this case, for measurement of specific surface area, it computed with the BET adsorption method using the Ohkurariken make and automatic specific-surface-area measuring device SIGMA-V.

[0020] Moreover, the Suzuki trading house PCT property measuring device was used for measurement of a hydrogen storage capacity. The sample cel with a volume of 5.3 cc was connected to the standard cell (26.3 cc) through the bulb, and after this equipment checked that close [of a sample] carried out several blank tests by putting a pressure on the cel which is not for 10 hours, and did not have leakage next, it put the sample (0.3-1g (0.3-1cm³)) in the sample cel, and heated it for 30 minutes at 10-3torr and 150 degrees C. After heating, after reducing the temperature of a sample cel to a room temperature, hydrogen was introduced into the sample cel from the standard cell (pressure: 5MPa). And from the pressure variation after hydrogen installation, the hydrogen storage capacity in a sample was calculated by count. In addition, the experiment was conducted at the room temperature (25 degrees C).

[0021]

[Table 1]

[0022] as shown in Table 1, the specific-surface-area value of the amorphous carbon of this invention was alike and small compared with the activated carbon of the example of a comparison, and at most 20-100m²/g thing which it is about 2/g, and the hydrogen storage capacity of amorphous carbon becomes more than twice compared with activated carbon, and is excelled in a hydrogen absorption property became clear.

[0023] (Example 2) The poly acene system oligomer compounded in the example 1 was set to the electric furnace, heat-treatment of 5 hours was performed with the sink at the programming rate of 20 degrees C / min, and the temperature of 300-900 degrees C, and natural radiationnal cooling of the Ar gas of 11. / min was carried out after that.

Moreover, using a resistance heating type vacuum pressure-sintering furnace as a thing of another heat history, 1000-2200 degrees C performed heat-treatment of 5 hours for the poly acene system oligomer compounded in the example 1, and what carried out natural radiationnal cooling was prepared as an object for a comparison.

[0024] (Example 3) It replaced with poly acene system oligomer, and Polly P-phenylene (PPP) was used as a generation raw material of amorphous carbon. Kovacic shown in the reaction formula (1) having shown this Polly P-phenylene (PPP) in next ** 1 -- it compounded from benzene by law -- {-- P. -- Kovacic, A.Kyriakis, J.Am.Chem.Soc., and 85 454(1963)}. Compounded PPP is obtained with a powder-like gestalt. And this PPP was set to the electric furnace, heat-treatment of 1 hour was performed with the sink at the programming rate of 20 degrees C / min, and 620,700 degrees C, and natural radiationnal cooling of the H₂ gas of 11. / min was carried out after that.

[0025]

[Formula 1]

[0026] (Example 4) In 400 degrees C, the pyrolysis of the petroleum system heavy oil

was carried out, and it considered as raw coke. Then, this raw coke was ground in mean particle diameter of 30 micrometers, and particle-like raw coke was obtained. Next, this raw coke was set to the electric furnace, heat-treatment of 1 hour was performed with the sink at the programming rate of 20 degrees C / min, and each temperature of 450-900 degrees C, and natural radiationnal cooling of the Ar gas of 11. / min was carried out after that. Moreover, what performed heat-treatment of 1 hour for raw coke at 1000-2200 degrees C was prepared as an object for a comparison, using a resistance heating type vacuum pressure-sintering furnace as a thing of another heat history.

[0027] Next, these carbon obtained according to the above-mentioned examples 2-4 was put into the container made from agate, and was ground, and the hydrogen storage capacity by the above-mentioned PCT property measuring device was calculated. The relation between a hydrogen storage capacity and heat treatment temperature is shown in drawing 1. Heat treatment temperature (degree C) was taken on the axis of abscissa, and the hydrogen storage capacity (vol%) is taken on the axis of ordinate.

[0028] The thing (example 2) using poly acene system oligomer is in an inclination with most hydrogen storage capacities so that drawing 1 may show. Consequently, as heat-treatment-temperature range Poly acene system oligomer (example 2), Polly P-phenylene (example 3), And in any [of petroleum raw coke (example 4)] case, it is more than 0.18vol%, and it increases the hydrogen storage capacity of the amorphous carbon obtained by heat-treating at 500-900 degrees C compared with activated carbon so that it may turn out that it compares with the data of Table 1.

[0029] (Example 5) The H/C ratio (ratio of the number of hydrogen atoms and a carbon atomic number) obtained by heat treatment of the poly acene system oligomer shown in examples 2-4, heat treatment of Polly P-phenylene, and heat treatment of petroleum raw coke produced a variously different amorphous carbon ingredient. And the number of hydrogen atoms in these carbon and the carbon atomic number were measured with the elemental-analysis equipment made from PerkinElmer (Model-240C), and also about the amount of hydrogen in the carbon with which heat treatment temperature was obtained above 1000 degrees C, it is the approach based on JISZ2614, and asked for them using Horiba EMGA621 based on an inert gas heat-of-fusion electric conductivity method.

[0030] After such elemental analyses dry a sample at 120 degrees C for about 5 hours, they are sampled in an aluminum cup in an argon ambient atmosphere, and are performed from the weight of CO₂ gas produced by combustion by calculating a hydrogen content from the weight of H₂O which generates a carbon content again.

[0031] The relation between H/C of amorphous carbon and a hydrogen storage capacity is shown in drawing 2 as the result. The H/C ratio was taken on the axis of abscissa, and the hydrogen storage capacity (vol%) is taken on the axis of ordinate. Consequently, although the thing using poly acene system oligomer shows too that there are most hydrogen storage capacities in the range where a H/C ratio is large from drawing 2, in any [of poly acene system oligomer, Polly P-phenylene, and petroleum raw coke] case, the H/C ratio shows that a hydrogen storage capacity becomes more than 0.18vol%, and increases compared with activated carbon with or more 0.05 0.45 or less amorphous carbon.

[0032] (Example 6) The H/C ratio chose the thing of 0.43-0.45 in each heat treatment article of the poly acene system oligomer created in the example 5, Polly P-phenylene, and petroleum raw coke, and the thing and H/C ratio of 0.17-0.19 found the distance

between layers of these amorphous carbon (d002) using the Rigaku wide angle X-ray diffractometer (RAD-B). When the carbon of measurement of the spacing (d002) of the field by the wide angle X diffraction (002) is powder, as it is, disintegration of the minute piece-like case is carried out with an agate mortar, it makes a line source CuKalpha monochrome-ized by the click and the graphite monochromator to the sample cell made from glass, and performs it by measuring a wide angle X diffraction curve on the strength with reflective type diffractometer. And d002 was calculated by the several 1 following Bragg equation from the wavelength lambda of include-angle 2theta in which a curve has a peak, and CuK alpha rays.

[0033]

[Equation 1]

[0034] The relation between the distance between layers (nm) of the field (002) of amorphous carbon and a hydrogen storage capacity (vol%) is shown in drawing 3 as the result. d002 (distance between layers) was taken on the axis of abscissa, and the hydrogen storage capacity (vol%) is taken on the axis of ordinate. Consequently, although the one where a H/C ratio is lower than drawing 3 shows that there are many high hydrogen storage capacities in the range where the distance between layers of d002 is broad, further, the H/C ratio in amorphous carbon increases [using activated carbon rather than / distance / between layers / hydrogen storage capacity / of a thing 0.4nm or more / 0.45 / or less / 0.05 or more], and, as for the predominance, the distance between layers is not accepted by the thing 0.35nm or less.

[0035] Alterations various in the range which is not limited to the above-mentioned gestalt of operation at all, and does not deviate from the meaning of this invention are possible for this invention. For example, although the raw coke from poly acene system oligomer, Polly P-phenylene (PPP), or petroleum system heavy oil was used as a generation raw material of amorphous carbon with the gestalt of the above-mentioned implementation, it is clear from the meaning of invention that the other natural high molecular compound, naturally-occurring polymers, or coal system raw coke can be used.

[0036]

[Effect of the Invention] Since the hydrogen absorption ingredient of this invention carries out occlusion of the hydrogen to the amorphous carbon according to claim 1 which whose specific surface area is below 400m²/g, and has a H/C ratio in the range of 0.05-0.45 like, it can increase the hydrogen storage capacity per volume rather than the thing using conventional activated carbon. Therefore, not only safety is high, but applying this hydrogen absorption ingredient to the fuel sources (hydrogen source of supply) in fuel cell systems, such as a source of mounted power or a small electric organ, does so the effectiveness that generating duration is extensible etc.

[0037] Moreover, by [according to claim 2] setting distance between carbon microcrystal layers of amorphous carbon to 0.4nm or more, or using [like] the amorphous carbon according to claim 3 which heated the high molecular compound etc. at 500 degrees C - 900 degrees C, and was obtained like, further, by [according to claim 4] performing the heating under an inert atmosphere, increase can plan a hydrogen storage capacity and the effectiveness of this invention will become still larger like.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the relation between the heat treatment temperature of the amorphous carbon generate time concerning this invention, and the hydrogen storage capacity of the obtained amorphous carbon.

[Drawing 2] It is drawing having shown the relation of the H/C ratio of amorphous carbon and hydrogen storage capacity concerning this invention.

[Drawing 3] It is drawing having shown the relation of the distance between d 002 layers and the hydrogen storage capacity of the amorphous carbon concerning this invention.

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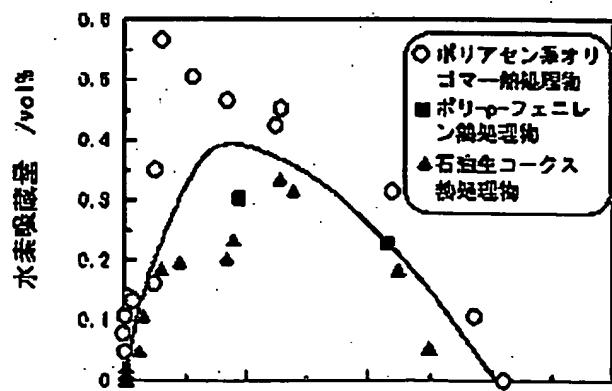
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(54)【発明の名称】 水素吸蔵材料

(55)【要約】

【課題】 体積当たりの水素吸蔵量の大きい水素吸蔵材料を提供すること。

【解決手段】 炭化水素の炭素粒晶子を含む層状構造の非晶質炭素の比表面積が $400 \text{ m}^2/\text{g}$ 以下であって、水素原子数と炭素原子数との比H/Cが0.05以上0.45以下の範囲にあり、この非晶質炭素の炭素粒晶子層間もしくは結晶子末端間に水素を吸蔵させたもので、非晶質炭素の(002)面の層間距離 d_{002} が0.4nm以上であること。高分子化合物、天然高分



特開2001-106516

2

えば、自動直用燃料電池の燃料源として用いた時に十分な走行距離が得られないといった問題があった。

【0006】本発明の解決しようとする課題は、このような自動直用燃料電池の燃料源などとしての利用が期待でき、軽量・豊富な資源を待つ炭素材料を活用するものであって体積当たりの水素吸蔵量の大きな水素吸蔵材料を提供することにある。

【0007】

【課題を解決するための手段】この課題を解決するために本発明の請求項1記載の水素吸蔵材料は、炭化水素の炭素結晶子を含む層状構造の非晶質炭素の比表面積が $400\text{m}^2/\text{g}$ 以下であって、水素原子数と炭素原子数との比H/Cが0.05以上0.45以下の範囲にあり、この非晶質炭素の炭素結晶子層間もしくは結晶子末端間に水素を吸蔵させてなることを特徴とする水素吸蔵材料。

【0008】上記非晶質炭素の炭素結晶子は主として炭化水素よりなり、六員環網状平面構造を有するものであり、その一部は結晶状の黒鉛と同様の層状構造を有している。また、上記結晶子の末端は炭素に対し、水素が結合した状態になっており、炭素結晶子の末端間に形成されたキャビティーに対しても水素分子は吸蔵される。このため、従来の物理吸着により炭素表面に水素が吸蔵される活性炭に比べ、本発明にかかる非晶質炭素はより多くの水素を吸蔵することができる。

【0009】この場合、本発明の非晶質炭素の比表面積は $400\text{m}^2/\text{g}$ 以下とした。この値は、通常の活性炭に比べ小さいため、高密度が大きくなつて、体積当たりの水素吸蔵量を多くできる。

【0010】また、非晶質炭素中の水素原子数と炭素原子数との比H/C(水素原子数/炭素原子数)が0.05よりも小さくなると水素吸蔵時に炭素結晶子の末端において生成する水素吸蔵量が小さくなる恐れがある。一方、H/C(水素原子数/炭素原子数)が0.45を越えると、炭素の六員環網状平面構造が極端に小さくなり、水素吸蔵サイトが減少してしまう。

【0011】そして本発明では、請求項2記載のように、前記非晶質炭素の炭素結晶子層間距離が 0.4nm 以上であることが望ましい。

【0012】層間距離が 0.4nm 以上とすることにより層間にスムーズに水素分子が吸蔵され、吸蔵量が増加

1

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【特許請求の範囲】

【請求項1】炭化水素の炭素結晶子を含む層状構造の非晶質炭素の比表面積が $400\text{m}^2/\text{g}$ 以下であつて、水素原子数と炭素原子数との比H/Cが0.05以上0.45以下の範囲にあり、この非晶質炭素の炭素結晶子層間もしくは結晶子末端間に水素を吸蔵させてなることを特徴とする水素吸蔵材料。

【請求項2】前記非晶質炭素の炭素結晶子層間距離が 0.4nm 以上であることを特徴とする請求項1記載の水素吸蔵材料。

【請求項3】前記非晶質炭素は、高分子化合物、天然高分子、石油または石炭から得られる生ゴーラスより選ばれた1種または2種以上の材料を 500°C 以上900°C以下の温度範囲で熱処理して得られたものである請求項1または2記載の水素吸蔵材料。

【請求項4】前記熱処理は不活性雰囲気下で行われたものであることを特徴とする請求項3に記載の水素吸蔵材料。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水素吸蔵材料に関するものである。

【0002】

【従来の技術】水素は、合成化学工業や石油精製などに多量に利用されている重要な化学原材である。一方、将来的エネルギー問題と環境問題を解決するために、クリーンなエネルギーとしての水素利用技術は重要な位置を占めると考えられ、水素製造、貯蔵、輸送、転換技術の各方面において活発に研究開発が進められている。水素の吸蔵・輸送技術においては、水素タンクなど極めて大規模な物を除き、いわゆる水素吸蔵合金が主要な役割を果たすと考えられている。特に燃料電池自動車などの移動媒体において電池などに水素を供給することが要求される。

【0003】このような要求に対しては、既存の技術である高圧水素ガスボンベや液化水素ボンベでは適応しないからである。このような場面で主役と考えられる水素吸蔵合金にも、合金であるが故の重さ(単位質量当たりの吸蔵量が小さい)、吸蔵-放出の繰り返しによる劣化

(3)

特開2001-106516

3

に、水素吸収量が大きく低下してしまう。また、上記熱処理温度が900°Cを越えた場合には、前述したH/Cが0.05よりも小さくなり、水素吸収時に炭素結晶子の末端において生成する吸収量が小さくなる恐れがある。さらに好ましい熱処理温度の下限は600°C、上限は800°Cである。

【0015】さらに本発明では、請求項4記載のように、上記加熱は不活性雰囲気中で行うことが好ましい。これにより、炭素原料の酸化を防止することができ、非晶質炭素を得ることができる。なお、上記不活性雰囲気としては、例えば、真空雰囲気、希ガス、N₂等よりも雰囲気等を挙げることができる。また、加熱の好ましい時間は特に限定されないが、その中でも30分間～8時間の範囲が特に好ましい。

【0016】

【発明の実施の形態】以下に本発明の実施例を詳細に説明する。

【0017】(実施例1) 理学器械製の高圧反応装置を用い、ジフェニルシアセチレンの高圧重合(0.1GPa, 250°C, 5h)により、ポリアセン系オリゴマーを合成した(Y. Kojima, M. Tsuji, T. Matsuoka, H. Takahashi, Macromolecules, 27, 3735 (1994))。かくして得られたオリゴマーを電気炉にセットし、1リットル/minのArガスを流しながら、20°C/minの昇温速度、600, 800°Cの各温度で5*

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*時間の加熱処理を行い、その後、自然放冷した。得られた非晶質炭素をめのう製容器に入れ、粉碎した。

【0018】(比較例1) 大阪ガスケミカル製の活性炭3種類(商品名: M15, M20, M30)を用いた。

【0019】上記実施例1の非晶質炭素2種類(600°C, 800°C)と、比較例1の活性炭3種類(商品名: M15, M20, M30)について、比表面積と水素吸収量を測定したので、その結果を表1に示す。この場合、比表面積の測定には、六角型研削、自動比表面積測定装置SIGMA-Vを用い、BET法により算出した。

【0020】また、水素吸収量の測定には、鈴木商館製PCT特性測定装置を用いた。この装置は、容積5.3ccのサンプルセルがバルブを介して標準セル(26.3cc)に接続されており、試料の入っていないセルに圧力を掛けることによる数回のプランクテストを10時間実施して漏れがないことを確認した後、次に、0.3～1g(0.3～1cm³)の試料をサンプルセルに詰め、10⁻³ torr, 150°Cで30分間加熱した。加熱後、サンプルセルの温度を室温まで低下させた後、水素を標準セルからサンプルセルに導入した(圧力: 5MPa)。そして水素導入後の圧力変化から、試料中の水素吸収量を計算により求めた。なお、実験は室温(25°C)で行った。

【0021】

【表1】

	熱処理温度	比表面積 (m ² g ⁻¹)	水素吸収量 (vol%)
(本発明品) 非晶質炭素	600°C 800°C	05.1 21.03	0.45 0.56
(比較品) 活性炭M15	—	1392	0.16
M20	—	2090	0.14

(4)

特開2001-106516

5

5時間の加熱処理を行い、自然放冷したものと比較用として用意した。

【0024】(実施例3)ポリアセン系オリゴマーに代えて、ポリ-P-フェニレン(PPP)を非晶質炭素の生成原料として用いた。このポリ-P-フェニレン(PP)は次の化1に示した反応式(1)に示すKovac c i c法によりベンゼンから合成した(P. Kovac i c. A. Kyriakis, J. Am. Chem. S*



【0026】(実施例4)石油系重質油を400°Cにおいて熱分解させ、生コークスとした。その後、この生コークスを平均粒径30μmに粉碎し、粒子状の生コークスを得た。次にこの生コークスを電気炉にセットし、1リットル/m inのArガスを流しながら、20°C/m inの昇温速度、450~900°Cの各温度で1時間の加熱処理を行い、その後、自然放冷した。また、別の熱履歴のものとして抵抗加熱式真空加圧焼結炉を用い、生コークスを1000~2200°Cで1時間の加熱処理を行ったものを比較用として用意した。

【0027】次に、上記実施例2~4によって得られたこれらの炭素をめのう製容器に入れ、粉碎し、前述のPCT特性測定装置による水素吸蔵量を求めた。図1には、水素吸蔵量と熱処理温度の関係を示す。横軸に熱処理温度(°C)を探り、縦軸に水素吸蔵量(v o 1%)を探っている。

【0028】その結果、図1よりわかるように、ポリアセン系オリゴマーを用いたもの(実施例2)が最も水素吸蔵量が多い傾向にあり、また熱処理温度範囲としては、ポリアセン系オリゴマー(実施例2)、ポリ-P-フェニレン(実施例3)、及び石油生コークス(実施例4)のいずれの場合も、500~900°Cで熱処理することによって得られた非晶質炭素の水素吸蔵量は0.18 v o 1%以上である。表1のデータと比較するとわかるように活性炭に比べ増加する。

【0029】(実施例5)実施例2~4に示したポリアセン系オリゴマーの熱処理、ポリ-P-フェニレンの熱処理、石油生コークスの熱処理により得られるH/C比(水素原子数と炭素原子数との比)が様々な非晶質

* o.c., 85 454 (1963)。合成されたPPPは粉末状の形態で得られる。そしてこのPPPを電気炉にセットし、1リットル/m inのH₂ガスを流しながら、20°C/m inの昇温速度、620, 700°Cで1時間の加熱処理を行い、その後、自然放冷した。

【0025】

【化1】

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※ガス融解熱電導度法に基づく堀場製作所製のEMGA 621を用いて求めた。

【0030】これらの元素分析は、サンプルを120°Cで約5時間乾燥した後、アルゴン雰囲気中でアルミニウムカップにサンプリングし、燃焼により生じるCO₂ガスの重量から炭素含有量を、また、発生するH₂Oの重量から水素含有量を求ることにより行われる。

【0031】図2には、その結果として非晶質炭素のH/Cと水素吸蔵量との関係を示している。横軸にH/C比を探り、縦軸に水素吸蔵量(v o 1%)を探っている。その結果、図2よりやはりポリアセン系オリゴマーを用いたものがH/C比の広い範囲において最も水素吸蔵量が多いことを示しているが、ポリアセン系オリゴマー、ポリ-P-フェニレン、石油生コークスのいずれの場合もH/C比が0.05以上0.45以下の非晶質炭素では水素吸蔵量は0.18 v o 1%以上となって、活性炭に比べ増加することを示している。

【0032】(実施例6)実施例5で作成したポリアセン系オリゴマー、ポリ-P-フェニレン、石油生コークスの各熱処理品の中でH/C比が0.17~0.19のものと、H/C比が0.43~0.45のものを選び、これらの非晶質炭素の層間距離(d₀₀₂)を理学器械の広角X線回折装置(RAD-B)を用いて求めた。広角X線回折による(002)面の面間隔(d₀₀₂)の測定は、炭素が粉末の場合はそのまま、微小片状の場合はめのう乳鉢で粉末化し、硝子製試料セルにつめ、グラファイトモノクロメータで草色化したCu K α を線源とし、反射式ディフラクトメータ法によって広角X線回折強度曲線を測定することにより行う。そして曲線がビ

(5)

特開2001-106516

7

る。その結果、図3より、H/C比が低い方が $d_{0.05}$ の層間距離の幅広い範囲で高い水素吸蔵量が多いことを示しているが、さらに非晶質炭素中のH/C比が0.05以上0.45以下で、層間距離が0.4nm以上のものの水素吸蔵量は活性炭を用いるよりも増加し、層間距離が0.35nm以下のものではその優位性は認められない。

【0035】本発明は上記した実施の形態に何ら限定されるものではなく、本発明の趣旨を逸脱しない範囲で種々の改変が可能である。例えば、上記実施の形態では、非晶質炭素の生成原料としてポリアセチルオリゴマー、ポリ-P-フェニレン(PPP)、あるいは石油系高質油からの生コーカスを用いたが、勿論それ以外の高分子化合物、天然高分子、あるいは石炭系生コーカスなどを用いることができるることは発明の趣旨から明らかである。

【0036】

【発明の効果】本発明の水素吸蔵材料は、請求項1記載のように、比表面積が $400\text{ m}^2/\text{g}$ 以下であってH/C比が0.05~0.45の範囲にある非晶質炭素に水素を吸蔵させるものであるから、従来の活性炭を用いた*

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*よりも体積当たりの水素吸蔵量を増大させることができる。したがってこの水素吸蔵材料を直駆動力源あるいは小型発電器などの燃料電池システムにおける燃料源(水素供給源)に適用することは、安全性が高いばかりでなく、発電時間を延長できるなどの効果を有するものである。

【0037】また、請求項2記載のように、非晶質炭素の炭素結晶子層間距離をり、4nm以上としたり、請求項3記載のように、高分子化合物などを500°C~900°Cで加熱して得られた非晶質炭素を用いることにより、さらに請求項4記載のように、その加熱を不活性雰囲気下で行うことにより、水素吸蔵量を増大が図れ、本発明の効果は一層大きいものとなる。

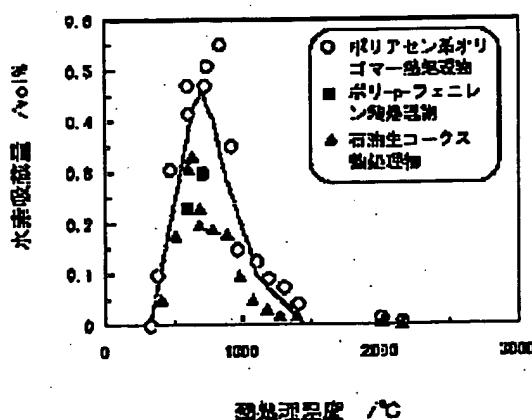
【図面の簡単な説明】

【図1】本発明に係る非晶質炭素生成時の熱処理温度と得られた非晶質炭素の水素吸蔵量との関係を示した図である。

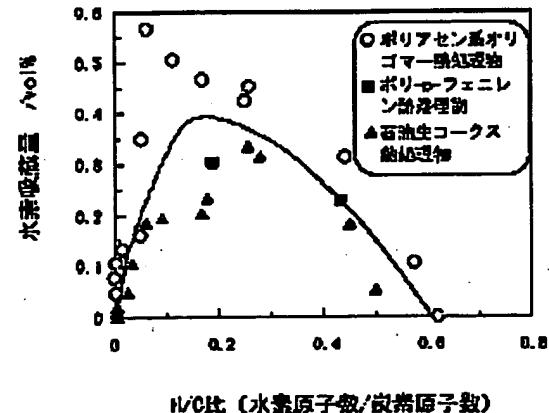
【図2】本発明に係る非晶質炭素のH/C比と水素吸蔵量との関係を示した図である。

【図3】本発明に係る非晶質炭素の $d_{0.05}$ 層間距離と水素吸蔵量との関係を示した図である。

【図1】



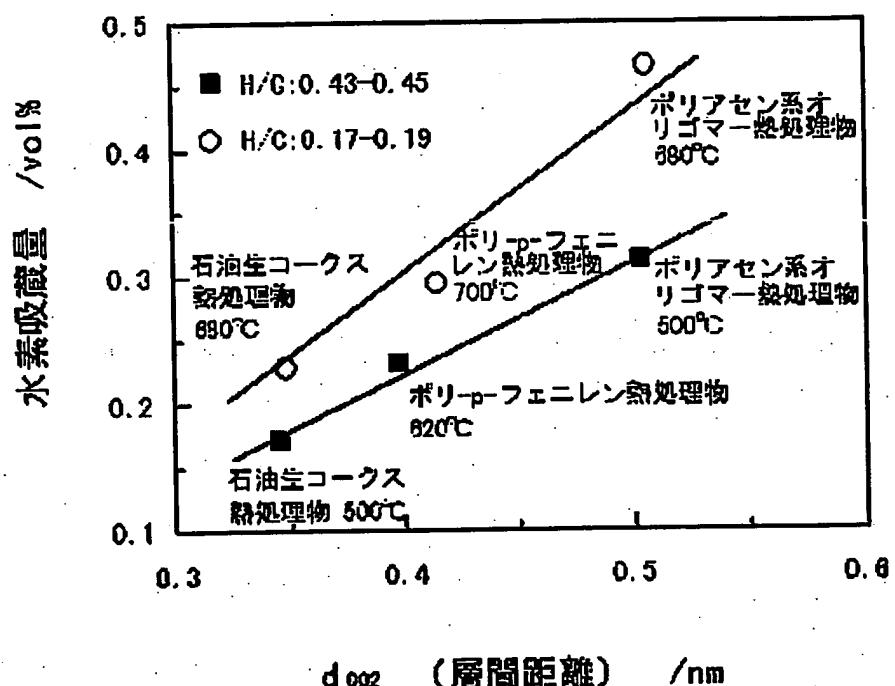
【図2】



(6)

特開2001-106516

【図3】



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